



Potential formation damage and mitigation methods using seawater-mixed acid to stimulate sandstone reservoirs



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ABSTRACT

It has been a practice to use seawater to prepare hydrochloric acid for carbonate reservoir stimulation in the offshore operations where fresh water is relatively expensive or logistically impossible to use. However, compare with carbonate matrix stimulation, F^- and secondary SiF_6^{2-} are released into the solution using hydrofluoric acid to treat sandstone reservoirs. The released components will combine with Mg^{2+} , Ca^{2+} , Na^+ , and K^+ ions in seawater. Large quantities and various types of precipitates are formed when critical scaling tendency was exceeded, which results in serious formation damage.

In this research, artificial simulated seawater (salinity about 35‰) was mixed with mud acid (almost hydrofluoric acid) and multi-hydrogen acid (an organophosphonic acid complex). Chemical effects of current seawater-mixed acid were investigated using spectrophotometry methods. The chemical effects include acid composition and concentration, HCl volume, seawater dilution ratio, and inorganic salt on damage quantities during acid preparation and reaction. Effective mitigation methods favorable to the inhibition of precipitation were provided.

Results show that fluoride precipitates including CaF_2 and MgF_2 can be effectively mitigated by decreasing the free F^- concentration and the pH value, increasing the seawater dilution and adding the inorganic electrolytes to elevate the ionic strength of solution. Because the organic phosphonic acid forms complexes with the metal ions, precipitation mitigation capacity of the multi-hydrogen acid is stronger than that of the mud acid. A special and abnormal common-ion effect was discovered based on the multi-hydrogen acid system. The addition of calcium ions in the seawater-mixed multi-hydrogen acid solution produces a super-clear liquid system with the turbidity <30 FTU. Static simulation shows that fluorosilicate precipitates as products of the secondary reaction in acidizing are mainly determined by the dissolution ratio. The precipitates can be mitigated by adding proper amount of hydrochloric acid, increasing the concentration of ammonium chloride in acid, and using appropriate inhibitors such as organophosphonic acid HA and DA. According to a parametric analysis, a seawater-mixed acid system based on the synergistic reactions of acid effect, salt effect and complex effect was proposed to mitigate formation damage for the sandstone reservoir stimulation using seawater-mixed acid. Reactions between the acid and different minerals indicate that this acid system could remain clear and eliminate secondary deposition during acidizing treatment.

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1. Introduction

Acidizing is one of the most commonly used methods to improve production and injection in offshore oilfields. In matrix treatment, water, acid and other additives used in the fluid preparation are all transported from the land. The volume of water used to prepare acid varies from a few dozen to 100 m³ for production

wells, and the number is about 100–150 m³ for injection wells. The transport of such large amounts of fresh water is inconvenient and expensive from the land to offshore platform (He et al., 2011). In addition, the oil recovery of offshore oilfields is usually only 18–25%, far lower than that of onshore oilfields. One method to improve water flooding efficiency is increasing acid volume and squeezing more acid into the deep formation. However, economic considerations concerning material and transportation have inevitably prohibited massive usage of the acid. Therefore, it is more viable to use local materials, seawater, instead of fresh water to

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prepare the acid fluid system for most of the offshore oilfields where fresh water is not adequately accessible.

Desulfurated seawater flooding has been used in offshore oilfields for a long time (Al-Rubaie et al., 1987; Lindlof and Stoffer, 1983; McCune, 1982; Yuan et al., 2016). A variety of seawater-mixed systems has been developed for drilling fluid, completion fluid and fracturing fluid (AlMubarak et al., 2016; Harris and van Batenburg, 1999; Willson et al., 2004; Yuan et al., 2015). Such working fluid could not react with rocks, and it is convenient to prepare the working fluid using seawater. However, seawater-mixed acid has not been well formulated for reservoir stimulation because they can react with minerals to form some precipitates which may cause formation damage. Berry et al. (2012) and He et al. (2012) proposed seawater-mixed acid fluids for carbonate reservoir individually. The inhabitation of calcium sulfate precipitation was the main target, because SO_4^{2-} in seawater can react with Ca^{2+} produced by carbonate rocks. The preparation of seawater-mixed acid is much more difficult for sandstone reservoir acidizing than that for carbonate rock reservoir due to complex acid and rock reactions. The risks and scale of potential formation damage during acidizing can be aggravated for sandstone.

The primary concern in acid preparation is that hydrofluoric acid can react with Ca^{2+} and Mg^{2+} in seawater and generate insoluble CaF_2 , MgF_2 . The existence of these precipitates determines if the acid solution can be injected into the formation. In addition, SiF_6^{2-} ion generated by the acid and rock reaction will combine with Na^+ and K^+ in seawater to cause secondary damage. The fluoride silicate precipitates are difficult to be mitigated due to the strong chemical stability (Frayret et al., 2006). Current study analyzes factors of precipitation in the acid preparation and reaction through the laboratory experiments. Effective methods were developed to reduce potential damage of seawater-mixed acid for sandstone reservoir.

2. Materials and methods

2.1. Materials

Multi-hydrogen acid mainly consisting of an organophosphonic acid (MH) and a fluoride salt (MF) was provided by China Oilfield Services Limited. Hydrofluoric acid, hydrochloric acid and inorganic salts, including sodium chloride, sodium sulfate, potassium chloride, ammonium chloride, calcium chloride, magnesium chloride and minerals like quartz, kaolinite, illite, montmorillonite were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Organophosphonic acid and polycarboxylic acid were purchased from Taihei Water Treatment Technologies Co., Ltd, Shandong, China.

2.2. Methods

2.2.1. Measurement of precipitates

Turbidity of solutions was measured by a SP-754 UV/Vis spectrophotometer (Shanghai Spectrum Instruments Co., Ltd, China) to calculate the precipitation volume. Standard solutions were prepared by mixing 5.00 mL hydrazine sulfate solution (10 g/L) and 5.00 mL hexamethylenetetramine solution (10 g/L) in a 100 mL volumetric flask. After 24 h, deionized water was added to dilute the mixture to 100 mL, and turbidity of this standard solution was considered as 400 FTU. Then 0, 0.5, 1.25, 2.50, 5.00, 10.00, 12.50 mL standard solutions were placed into volumetric flasks of 50 mL and deionized water was added to the marked level. Consequently, a series of standard turbidity points was obtained as 0, 0.4, 10, 20, 40, 80, 100, 400 FTU. The series of standard solutions were put into polystyrene colorimetric wares (10 mm × 10 mm), and spectrophotometer was used to measure absorbance at the 680 nm

wavelength. The linear fitting of the standard curve was obtained (Fig. 1), and the relationship between turbidity and absorbance was:

$$\text{Turbidity} = 698.205 \times \text{Absorbance} \quad R^2 = 99.84\% \quad (1)$$

The turbidity of samples was calculated according to Equation (1) after measuring the absorbance. The aforementioned experiment method is simple and rapid to obtain accurate and reproducible data, and the procedure of diluting the solution or other pretreatment is not required. Therefore, it is especially suitable for strongly acidic and concentrated solution.

In this research, two types of acid including hydrofluoric acid (1.4% HF) and multi-hydrogen acid (2% MH and 2% MF) were respectively mixed with seawater. A series of single factor experiments were conducted to study the effect of acid types, fluoride concentration, HCl concentration, dilution ratio of seawater, and inorganic salt on precipitation volume in the preparation process of seawater-mixed acid: (1) Multi-hydrogen acid containing 2% MF and 2%–4% MH, and hydrofluoric acid containing 1.4% HF were prepared by using the simulated seawater. The turbidity change of each solution was periodically measured by the method above. (2) 2% MH was maintained for multi-hydrogen acid in the follow-up experiments, and fluoride concentration of both seawater-mixed acids was varied from 0.1% to 4.75%. (3) As another important factor for precipitation, 0.1%–5% HCl was added into seawater-mixed hydrofluoric acid and multi-hydrogen acid. (4) The seawater and the deionized water are mixed in different ratio to prepare the seawater-mixed acid. (5) Five types of inorganic salts in a wide range of concentration (0.5%–15%), including NaCl, KCl, CaCl_2 , MgCl_2 , NH_4Cl , were added respectively into the seawater-mixed acids. (6) After sealing for 12 h at room temperature, the turbidity of each solution mentioned above was determined.

2.2.2. Dissolution ability test

Dissolution ability test was conducted to simulate the reaction of acid and rocks. Mineral powder such as quartz, kaolinite, illite, montmorillonite were grinded into powder (100–120 meshes) and mixed with acids in plastic bottles. The ratio of powder mass to acid volume is 1:20. Caps were screwed tightly and the bottles were placed in 70 °C shaking water bath. One bottle was periodically taken and sampled to measure the dissolution percentage of minerals through mass loss method. Spent acids were filtered by two layers of filter paper and washed by deionized water. Then residual rock powder was dried in a 105 °C oven and weighted. The dissolution ratio of the acid was calculated according to the mass loss of

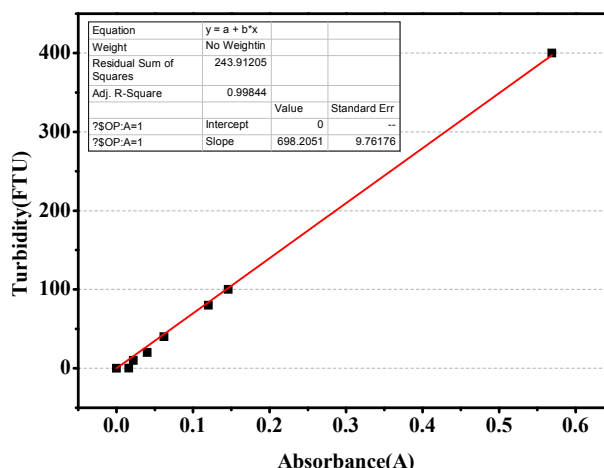


Fig. 1. Standard curve of turbidity and absorbance.

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